

## Preparation and Characterization of Some Transition Metal Complexes with ( N ,S ,O) New Schiff Base Ligand

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### Abstract:

The New Schiff base ligand 4,4'-[(1,1'-Biphenyl)-4,4'-diyl,bis-(azo)-bis-[2-Salicylidene thiosemicarbazide](HL)(BASTSC) and its complexes with Co(II), Ni(II), and Cu(II) were prepared and characterized by elemental analysis, electronic, FTIR, magnetic susceptibility measurements. The analytical and spectral data showed, the stoichiometry of the complexes to be 1:1 (metal: ligand). FTIR spectral data showed that the ligand behaves as dibasic hexadentate molecule with (N, S, O) donor sequence towards metal ions. The octahedral geometry for Co(II), Ni(II), and Cu(II) complexes and non electrolyte behavior was suggested according to the analysis data.

**Key words:** Schiff- base; Metal chelate complexes, octahedral geometry.

### Introduction

Metal complexes of Schiff base are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal atoms[1]. Schiff bases are generally bi-or tridentate ligands capable of forming very stable complexes with transition metals.

Thiosemicarbazones (TSCs) have received considerable attention because of these compounds which took part a wide spectrum of medicinal properties, including activity against tuberculosis, leprosy, and bacterial and viral infections[2,3]

This work describes the preparation and characterization of new Schiff base ligand (BASTSC) derived from thiosemicarbazone with Co(II), Ni(II), and Cu(II) metal ions by available techniques.

melting point of the ligand and its complexes. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra were recorded using KBr discs in 4000-400  $\text{cm}^{-1}$  range on FT-IR Shimadzu Spectrophotometer model 8400. Uv-Vis spectra were recorded in ethanol on Shimadzu Spectrophotometer double beam model 1700 Uv-Vis spectrophotometer.

Magnetic Susceptibilities were measured as powder samples using Faraday method, a Balance Magnetic MSB-MKI was employed for this purpose. The diamagnetic corrections were made by Pascal's constants[4]. Molar conductance measurements were determined in DMF by using an Alpha Digital conductivity meter model 800.

### Materials and Methods:

The electro thermal melting point model 9300 was used to measure the

### Preparation of Schiff base ligand (BASTSC)

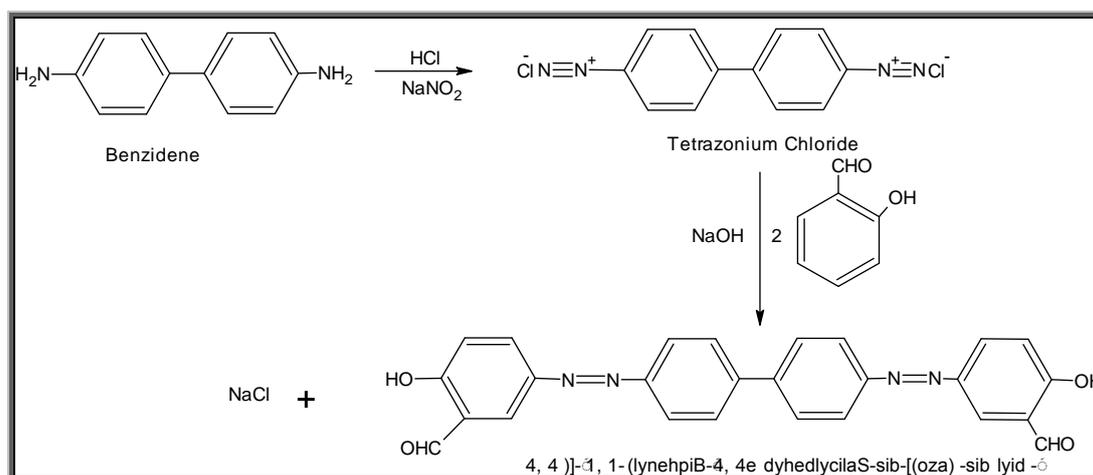
**The ligand was prepared as follows:**

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### 1. Preparation of the New tetrazo dye.

The new diazo dye (BAS) was prepared using the following method; tetrazoinum chloride solution was prepared by dissolving (1.840g, 0.01mol) of benzidine in 50ml of water and 4ml of concentrated hydrochloric acid. The solution was treated with 5ml of aqueous (1M) sodium nitrite drop wise and stirred for

30min. at 0C°, Salicyladehyde (2.44g, 0.02mol) was dissolved in 200ml of ethanol, and 80ml of 10% sodium hydroxide was added. The tetrazoinum chloride solution prepared above was then added drop wise for coupling, the mixture was stirred for 3 h at 0-5 C°, the product was filtered, dried and recrystallized twice from hot ethanol then dried in the oven at 100C° for 2 hours, Scheme 1.

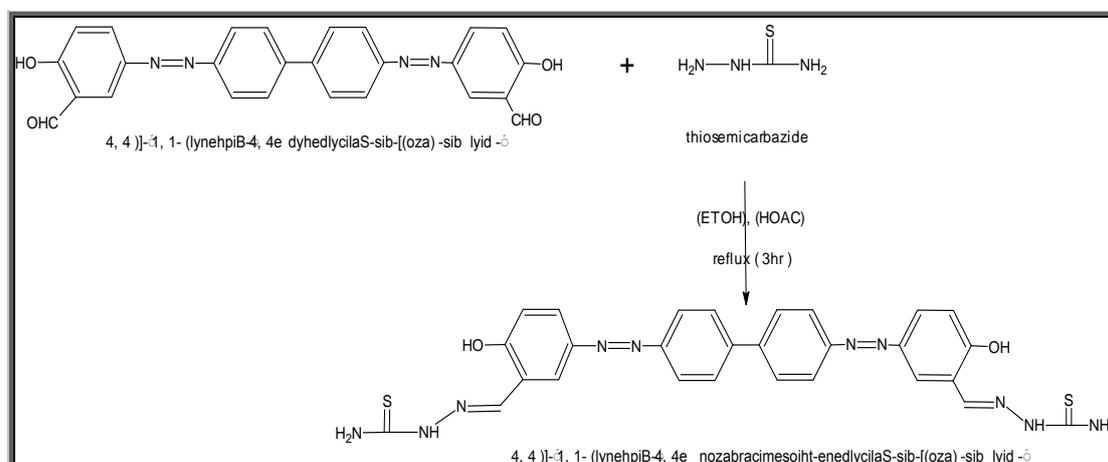


Scheme. 1: Preparation of the compound (BASTC).

### 2. Preparation of the Schiff base ligand.

The New Schiff base ligand (BASTSC) was prepared by condensation of (BAS) and thiosemicarbazide in equimolar (1:2) mole ratio, in absolute alcohol. Few

drops of glacial acetic acid were added to the reaction mixture and refluxed for 3 hrs. The product was recrystallized from ethanol, and dried over anhydrous CaCl<sub>2</sub>. The reaction mixture gave one product, m.p(150-153C°).



Scheme. 2: Preparation of the ligand (BASTSC).

### Preparation of metal complexes

The Schiff base ligand (1mmol) dissolved in absolute ethanol (25ml), mixed with salts of Co(II), Ni(II), and Cu(II) (1mmol) of each dissolved in ethanol (25ml). The reaction mixture was refluxed for 1h. The product was isolated after reduction of volume by evaporation. It was filtered off, washed with ethanol and dried under vacuum. The complexes obtained are listed in Table (1).

### Results and Discussion

The reactions of Co(II), Ni(II), and Cu(II) salts solutions with 4,4'-[(1,1'-Biphenyl)-4,4'-diyl,bis-(azo)-bis-[2-Salicylidene thiosemicarbazide] (HL) resulted in the formation of complexes. The complexes were crystallized as solids, which decomposed at high temperature. Physical and analytical data of the ligand and its complexes are listed in Table (1).

**Table 1: Physical and analysis data of ligand and its complexes**

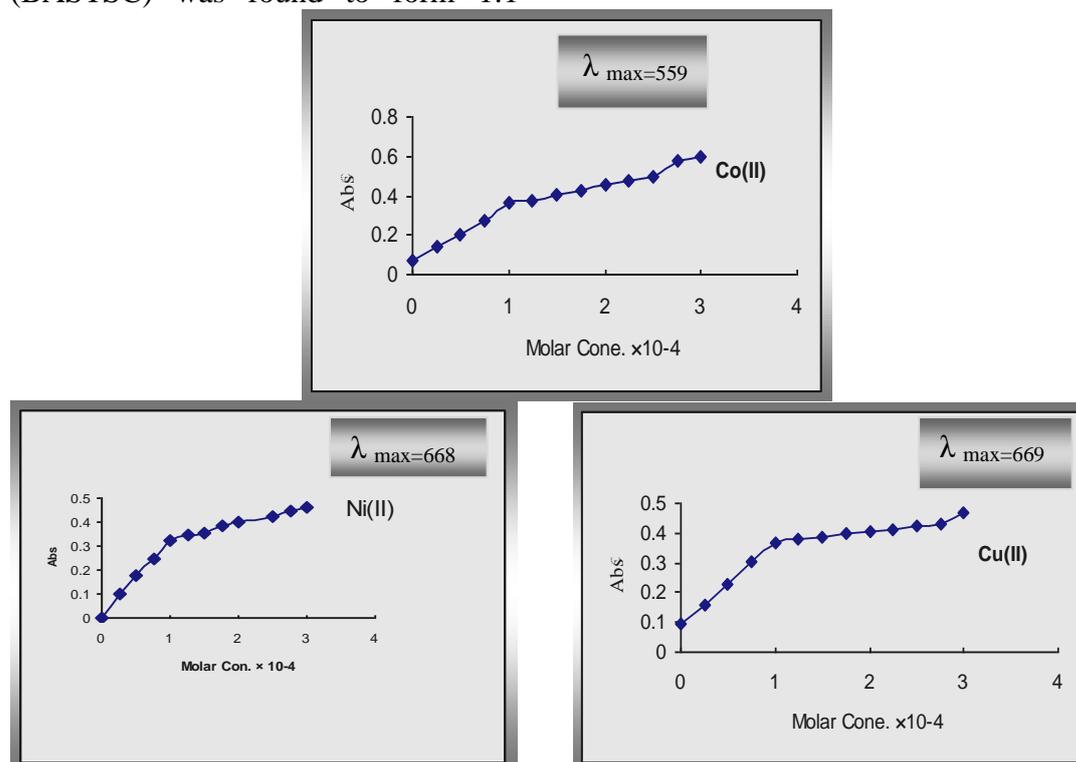
No.	Compound	Colour	M.P °C	Yield %	Formula	Found,(calc.)%			
						C	H	N	M
1	L=(ABSTSC)	Yellow	150-153	72	[C <sub>28</sub> H <sub>24</sub> N <sub>10</sub> O <sub>2</sub> S <sub>2</sub> ]	56.37 (55.33)	4.69 (4.89)	23.48 (24.32)	---- ----
2	[Co <sub>2</sub> L <sub>2</sub> ]	Green	300 d	66.23	[C <sub>56</sub> H <sub>44</sub> N <sub>20</sub> O <sub>4</sub> S <sub>4</sub> Co <sub>2</sub> ]	50.69 (51.89)	3.31 (3.58)	21.12 (22.68)	10.38 (9.84)
3	[Ni <sub>2</sub> L <sub>2</sub> ]	Green	290 d	72.43	[C <sub>56</sub> H <sub>44</sub> N <sub>20</sub> O <sub>4</sub> S <sub>4</sub> Ni <sub>2</sub> ]	50.70 (52.01)	3.31 (3.52)	21.12 (22.38)	10.36 (10.24)
4	[Cu <sub>2</sub> L <sub>2</sub> ]	Green	210 d	75.12	[C <sub>56</sub> H <sub>44</sub> N <sub>20</sub> O <sub>4</sub> S <sub>4</sub> Cu <sub>2</sub> ]	51.09 (52.89)	3.34 (2.12)	21.29 (20.54)	9.66 (10.22)

**L = Ligand, d= complex metal with decomposition**

### Metal : Ligand Ratio

The metal: ligand ratios of chelates were determined by the molar ratio method at the wavelengths of maximum absorption. The ligand (BASTSC) was found to form 1:1

chelates with metal ions under study, these results are in agreement with the values reported for some Schiff base complexes[5].Fig 1.

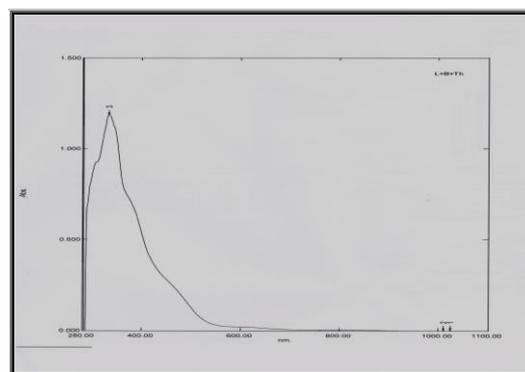


**Fig (1) :Mole ratio method for Co(II), Ni(II) and Cu(II) ions.**

### Magnetic and Electronic Spectral studies.

The magnetic moments and electronic spectral bands of the complexes are summarized in Table (2). The magnetic moment of cobalt (II) complex (4.23 B.M) suggests a high-spin octahedral geometry[6]. The electronic spectrum of this complex showed three absorption bands at ( $14810\text{ cm}^{-1}$ ),  $16546\text{ cm}^{-1}$  and ( $23853\text{ cm}^{-1}$ ), assigned to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ )  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)$  ( $\nu_3$ ) transition respectively, which are characteristic of octahedral stereo geometry[7]. For the nickel (II) complex, its magnetic moment (3.16 B.M), and d-d spectrum of this complex showed bands at  $14564$  and  $21413\text{ cm}^{-1}$ , which are suggesting the existence of  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  ( $\nu_2$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ) transitions with an octahedral spatial configuration[6].

The magnetic moment value of the copper (II) complex (1.82 BM) which may suggest an octahedral structure, Its electronic spectrum shows a band centered at  $15985\text{ cm}^{-1}$  which may assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition in octahedral environment[8]. The electronic spectra of the ligand and the Co(II), Ni(II), and Cu(II) complexes are shown in Figure 2. The electronic transitions, magnetic properties and conductivity values of the ligand and its complexes are listed in Table (2).



Ligand

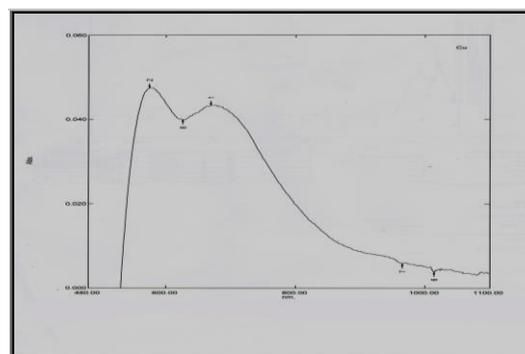
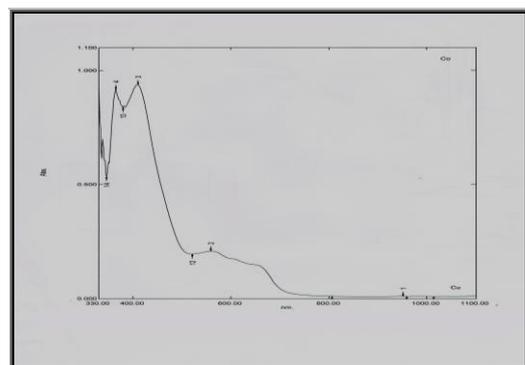
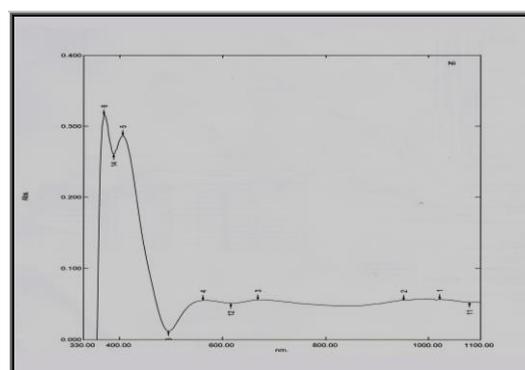
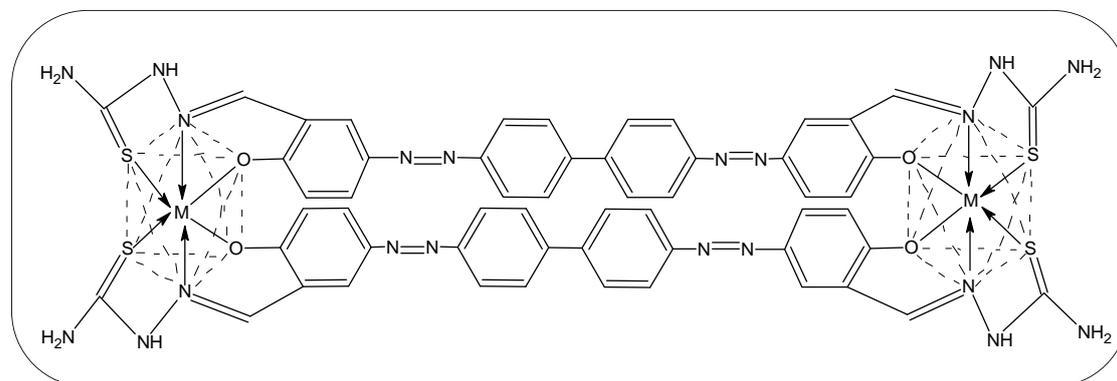
 $\text{Cu}_2\text{L}_2$  $\text{Co}_2\text{L}_2$  $\text{Ni}_2\text{L}_2$ 

Fig.(2). Electronic spectrum of the ligand(BASTSC) &  $[\text{M}_2\text{L}_2]$

### Molar Conductivity Measurements

All chelate complexes prepared in this work showed conductivity values ranged between (4.61-6.74)  $S. mol^{-1}.cm^2$ , in the DMF at room temperature

, all these complexes are non-electrolytic species[9]. The structural formula of complexes may be proposed as in Fig 4.



M= Co(II), Ni(II), and Cu(II)

Fig. 4: The proposed structural formula of the metal chelate complexes.

Table 2 : Electronic spectra, conductivity and magnetic moment of complexes

Complexes	Absorption Bonds( $cm^{-1}$ )	Transition	Conductivity $S.mol^{-1}. cm^2$	$\mu_{eff}(B.M)$
[Co <sub>2</sub> L <sub>2</sub> ]	14810 16546 23853	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$	6.74	4.23
[Ni <sub>2</sub> L <sub>2</sub> ]	14564 21413	$^3A_{2g} \rightarrow ^3T_{1g}(F)$ $^3A_{2g} \rightarrow ^3T_{1g}(P)$	4.61	3.16
[Cu <sub>2</sub> L <sub>2</sub> ]	15985	$^2E_g \rightarrow ^2T_{2g}$	5.21	1.82

### Infrared Spectra

The important infrared spectral bands for the synthesized ligand and its chelate complexes are given in Tabl(3). The ligand contains three potential donor sites: (1) the hydroxylic oxygen ,(2) the azomethine nitrogen , and (3) the thione sulfur . The absorption band at  $3373 cm^{-1}$  in the spectrum of ligand was attributed to (O-H)[10] while it is not observed in the spectra of the complexes, suggesting deprotonation of the hydroxyl group and a new band showed at (549-540) due to (M-O)[11,12].

The weak band in the spectrum of free ligand observed at  $3200 cm^{-1}$  due to (NH<sub>2</sub>) [13,14]. In the infrared spectra ,the free ligand exhibits a broad band at  $3263 cm^{-1}$  assignable to the (N-H) group[15,16]. Band near  $1645 cm^{-1}$

in the free ligand is assigned to (C=N). This band was shifted to lower wave number in the complexes due to the coordination of the nitrogen atom of the azomethine group[17]. On the other hand, the (C=S) band at  $1165 cm^{-1}$  in the free ligand was shifted to a lower frequency ( $1151-1116 cm^{-1}$ ) in the complexes spectra, which means that the shifts are due to coordination of ligand to metal atom by the thione sulfur group[18,19]. Also,the free ligand exhibits a band at  $1405 cm^{-1}$  assignable to the (N = N) group remained unaffected after complexation[20].

The spectra of all complexes showed new bands at about (474-466),(457-440) and (549-540)  $cm^{-1}$  attributed to  $\nu(M-N)$ ,  $\nu(M-S)$ , and  $\nu(M-O)$  coordination, respectively.

This represents a further evidence for the coordination of the ligand through both azomethine nitrogen, thione sulfur

and oxygen atoms[21,22] are presentative example for their spectra is given in Fig 3.

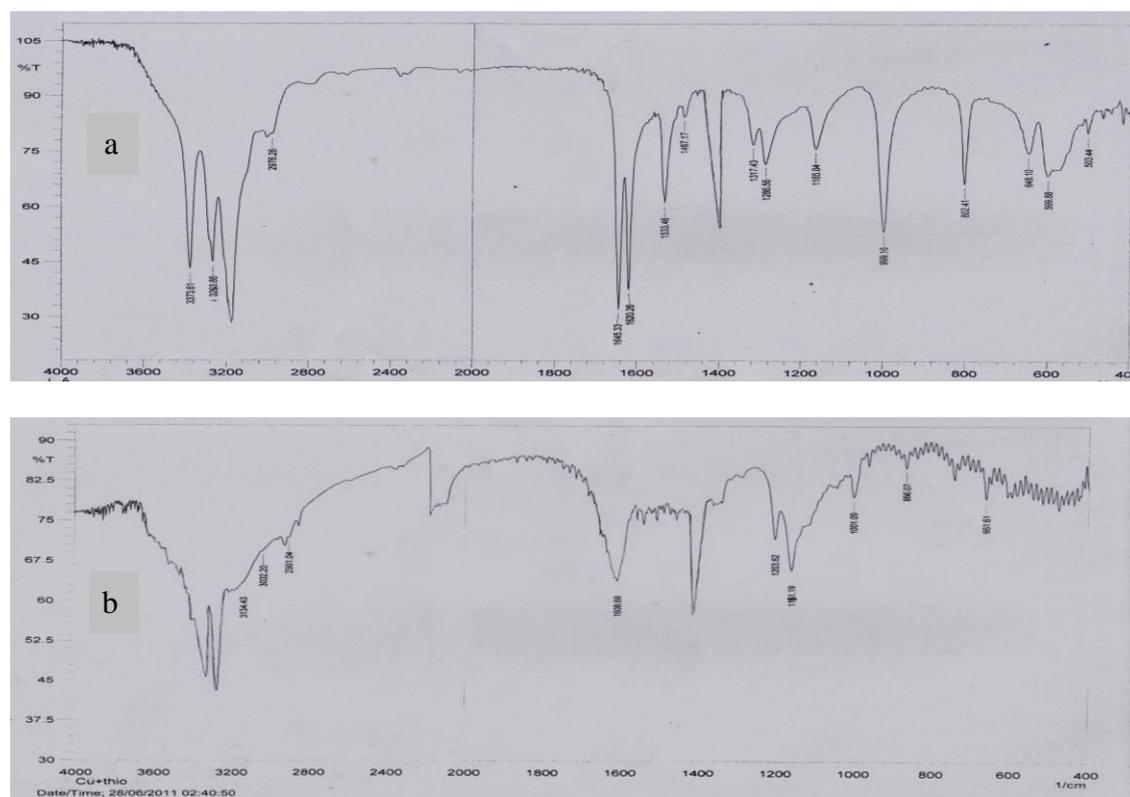


Fig 3. IR spectra of; (a) the ligand and (b)  $[Cu_2L_2]$

Table 3 : IR spectra frequencies for the ligand and its metal complexes in  $cm^{-1}$

Compound	$\nu$ (OH)	$\nu$ ( $NH_2$ )	$\nu$ (NH)	$\nu$ (C=N)	$\nu(N=N)$	$\nu(C=S)$	$\nu(NH-C=S)$	$\nu$ (M-O)	$\nu$ (M-N)	$\nu$ (M-S=C)
L=(ABSTSC)	3373 w	3200 w	3263 w	1645s	1405w	1165 s	802 m	----	----	-----
$[Co_2L_2]$	-	3150 w	3410 wbr	1600m	1404w	1116 m	866 w	549w	474 w	457 w
$[Ni_2L_2]$	-	3230 m	3410 w	1605s	1407w	1116 w	860 w	540w	466 w	447 w
$[Cu_2L_2]$	-	3260 w	3240 w	1608m	1404w	1151 m	866 w	547w	470w	440w

L= ligand, s = strong, w = weak, m = medium, br = broad

### References:

1. Raman N, Dhavethu JR .2007. A series of copper(II) complexes of mixed ligands with Schiff bases, Indian J. Chem. 46A: 1611-1614.
2. Hitoshi T, Tamao N, Hideyyki A, Manabu F, Takayuki M. 1997. Preparation and characterization of novel cyclic tetranuclear manganese (III) complexes, Polyhedron, 16: 3787.
3. Raman N, Thalamuthu S, Dhavedhuraja J, Neelakandan MA, Sharmila Banerjee. 2008. DNA cleavage and antimicrobial activity studies on transition metal(II) complexes of 4-aminoantipyrine derivative, J. Chilian Chem. Soc. 53N.
4. Eid A, Omer M, Khansa S. 2010. Synthesis and Characterization of Dinuclear Metal Complexes

- Stabilized by Tetradentate Schiff Base Ligands, American J. Appl. Sci. 7(5): 628-633.
- Poonam S, Deshmukh, Amit R, Jayshree N, Anand S. 2010. Synthesis, Characterization and Thermogravimetric studies of Some Metal Complexes with N<sub>2</sub>O<sub>2</sub> Schiff base ligand, World Appl. Sci. J. 9(11): 1301-1305.
  - Figgis, B N, and Lewis, J.1964. Progress in Inorganic Chemistry; Interscience, New York 37(6): 141-153.
  - Lever, A B P. 1968. Crystal Field Spectra. Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, London, New York, The Netherlands, 225- 243.
  - Nicholas, D .1973. Pergamon Texts in Inorganic Chemistry. Pergamon Press. Oxford. 1<sup>st</sup> Ed. 24, 1152-1154.
  - Ali.A. M. 2004. Synthesis and Characterization of Some Metal Complexes with New ligand 2-[(6-Ethoxy-2-Benzothiazolyl) Azo]-4- Benzyl Phenol (EBTAE), Sci. J. Baby Univ., 9, 841.
  - Lotf, A.S. ; Aminkhani A. ; Ersha,S. d, Karimnezhad, C; Chammamy S. and Kabiri, R.2008. Molecules. 13 .804-812.
  - Lever ABP. 1984. Inorganic Spectroscopy, 2<sup>nd</sup> edn (Elsevier Science Publisher, Amsterdam).
  - Demetgul C, Karakaplan M, Serin S and Digrak M. 2009. Synthesis characterization and biological properties of Ni(II), Co(II) and Cu(II) complexes of Schiff bases derived from 4-aminobenzylamine. J Coord. Chem. 62: 3544.
  - El-ajaily M, El-Ferjani R and Mailhub A, 2007. Preparation and Physical Investigation of Complexes Derived from 4-Dimethylaminobenzaldehyde and 4-Aminoantipyrine Schiff base with Ni(II), Cu(II), Rh(II), and Pt(IV) ions. Jordan J. chem. 2(3):287-296.
  - Nakamoto K.1976. Infrared and Raman Spectra of Inorganic and Coordination Compound; John Wiley and Sons, Newyork; 3<sup>rd</sup> .121-132.
  - El-Sonbati A, El-Bindary A, Rashed I. 2002. Polymer complexes XXXVII novel models and structural of symmetrical poly-Schiff base on hetero-binuclear complexes of dioxouranium (VI), Spectrochimica Acta Part A. 58:1411-1424.
  - Mubarak A, El-Assiery S. 2004. Supramolecular structures and properties models of macrocyclic polymer complexes, Appl. Organometal. Chem. 18: 343-352.
  - Nag J, Das D, Pal S, Sinha C. 2001. Synthesis and spectral characterization of homo-and hetero-dinuclear complexes with anew septadentate Schiff base ligand. Proc. Indian Acad. Sci. (Chem. Sci). 113: 11-20.
  - Sathisha M , Revankar V. Pai K .2008. Metal – Basad Dugs.11
  - Offiong O, Martelli S. 1997. Transition Metal. Chem. 22. 263.
  - Al-Adely K. 2000. Synthesis and Spectroscopic Study of Group (IIB) and (IIIB) Metalion Complexes with New Azo Compounds and with 1-(2-Pyridylazo)-2-Naphta. Ph. D. thesis, Baghdad University.
  - Chandra S, Tyagi V P and Raizada S. 2003. Synth. React. Inorg. Met-Org. Chem. New York, 2. 147-152.
  - Achut S, Amarnath N, Sarikam M, and Trimakk K. 2010. Synthesis, characterization and thermal study of some transition metal complexes of an asymmetrical tetradentate Schiff base ligand: J. Serb.Chem. Soc. 11.

## تحضير وتشخيص معقدات بعض العناصر الانتقالية مع ليكاند قاعدة شف الجديدة المانحة من (N, S, O)

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### الخلاصة :

تضمن البحث تحضير ثلاثة معقدات فلزية لايونات الكوبلت (II) ، النيكل (II) والنحاس(II) مع ليكاند قاعدة شف الجديد

4,4'-[(1,1'-Biphenyl) -4,4'- diyl, bis - (azo) - bis- [2- Salicylidene thiosemicarbazide] .  
شخصت بوساطة التحليل الدقيق للعناصر والأطياف الالكترونية وأطياف الأشعة تحت الحمراء والحساسية المغناطيسية . بينت نتائج الدراسة ان الليكاند يسلك كليكاند ثنائي الشحنة السالبة سداسي المخلب (O, S, N) يرتبط مع الايونات بنسبة مولية (1:1) (فلز : ليكاند). تم اقتراح الصيغة التركيبية ثمانية السطوح للمعقدات الصلبة وقد تبين أنها عديمة التوصيل الكهربائي.